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(54) Title: CAST DETERSIVE SYSTEMS

(57) Abstract

A general purpose detersive system and detersive system useful in warewashing and in laundry processes have been developed in which highly active encapsulated halogen sources have been incorporated into cast, solid detersive systems containing oxidizable organics that are highly reactive with the active chlorine sources. The stability of the detersive systems thus formulated has been shown to be sufficient to permit the cast materials to be storage stable for a sufficient period to permit the manufacture, distribution, sale and consumption of the cast materials before the availability of either the organic materials or the active halogen drops below an effective level.

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CAST DETERSIVE SYSTEMS

Field of the Invention

The invention relates to a detersive system containing soil removing detergents, an encapsulated halogen source and an organic component such as a polyalkylene oxide polymer, and to the use of the system in cleaning. More specifically the detersive systems of the invention can contain an active encapsulated halogen source and organic component, preferably an alkylene oxide polymer, which are co-stable at relatively high concentration during manufacture, storage, distribution, sale and use. Such detersive systems can be used in a variety of environments including general purpose cleaning, laundry, warewashing, etc., while producing an effective concentration of active chlorine for stain removal and sanitizing purposes in the presence of organic materials such as defoamers, soil removing nonionic surfactants and other polyalkylene oxide polymers.

Background of the Invention

Detersive systems have been used for many years in cleaning environments such as laundry, warewashing, hard surface cleaning and other general cleaning applications. Typically detersive systems are concentrates comprising mixtures of cleaning ingredients that, just prior to use, are mixed with water to form a cleaning medium or final use composition.

Many detersive systems contain organic materials that function in a variety of modes. Such organics can act as defoaming agents, dispersing agents, soil removing surfactants, thickening agents, casting aids, anti-redeposition aids, viscosity modifiers, brightening agents, etc. One important class of organic materials is polyalkylene oxide polymers. The polyalkylene oxide polymers derive their properties from the presence of large polymeric units derived from ethylene oxide, propylene oxide, heteric polymers thereof or block copolymers

thereof.

In a variety of use environments for such detersive systems, the presence of oxidizing available halogen such as chlorine or bromine can be important. Such halogen compounds can clean and remove certain residues, and can remove stains by oxidizing and destroying color generating functional groups in organic molecules. Further, the presence of sufficient concentrations of active chlorine can kill microorganisms and provide an antimicrobial or sanitizing action. However, detersive systems manufacturers have been reluctant to produce detersive systems in which organic materials such as polyalkylene oxide polymers and active chlorine yielding substances come into direct contact. Such contact can have undesirable safety and performance consequences.

In the manufacture of a variety of detersive systems, contacting many organic substances with active chlorine compounds is hazardous. At elevated temperatures or at high concentrations, contacting such organic compounds with active chlorine-yielding substances can result in a rapid reaction between the chlorine substances and the organic materials resulting in the production of large volumes of smoke or fire. If the detersive systems are successfully manufactured without rapid reaction between the chlorine and polyalkylene oxide components, the materials during manufacture, packaging, storage, distribution, sale and use can slowly react causing a significant depletion in the concentration of both the organic materials and the active chlorine substance. Such reactions commonly occur at a rate such that the concentration of active chlorine in the detersive system is below the concentration necessary for sanitizing properties and even is often below the concentration required for stain removal. Further such reactions can reduce the concentration of the organic materials to a level that results in substantially reducing the level of properties derived from the polymer.

We have found that active halogen can be lost through

a spontaneous degradation of active chlorine and by reactivity of chlorine with functional groups commonly found in organics used in detersive systems. The common functional groups reactive with active chlorine compounds include olefinic bonds commonly found in unsaturated fatty acids which are a common composition of alkali metal soaps, hydroxyl groups typically found in organic builders, amine groups, ether groups common in polyalkylene oxide polymers and aromatic rings typically found in alkyl benzene sulfonates, alkyl phenol ethoxylates, etc. The prior art commonly kept the concentration of organics less than 5 wt-% to reduce the harmful effects of the organic/chlorine interaction.

Accordingly a substantial need exists in the art for detersive systems containing significant effective concentrations (greater than 5 wt-%) of organic materials in the form of surfactants, foam suppressing agents and other functional materials, and containing effective concentrations (greater than 5 wt-%) of active chlorine from chlorine yielding compounds.

Brief Description of the Invention

We have found that a cast, solid detersive system containing an effective amount of a source of alkalinity, an effective hardness sequestering agent, at least 5 wt-% of an encapsulated source of chlorine and at least 5 wt-% of an organic such as polyalkylene oxide polymer is an effective detersive system that can be used in general purpose cleaning, laundry, warewashing, hard surface cleaning and sanitizing, and a variety of other end uses. We have surprisingly found that such materials when cast in a solid form result in substantial stability of an effective concentration of both chlorine and organic materials during manufacture, storage, distribution and use. We have found that for periods typical in the lifetime of such a product, the products can maintain a substantial concentration of active chlorine and an effective concentration of organics until the product is

entirely consumed.

Detailed Discussion of the Invention

The detersive systems of the invention can comprise an effective amount of a source of alkalinity, an effective amount of a hardness sequestering agent, at least 5 wt-%, up to about 50 wt-%, of an encapsulated source of chlorine compound, and at least 5 wt-%, up to about 50 wt-%, of an organic composition such as a polyalkylene oxide polymer. The detersive systems of this invention are typically in the form of a cast, solid material wherein the material is in the form of a large, solid mass having a minimum weight of about 50 grams held within a disposable container. The detersive system or concentrate can be dispensed from the container or can be removed from its container and placed into the dispenser for dilution and use at the use site.

Inorganic Source of Alkalinity

The detersive systems of the invention can contain an inorganic source of alkalinity. Sources of alkalinity identified as being useful in combination with the other components of the detersive systems of the invention include but are not limited to the following: alkali metal hydroxide, alkali metal phosphate, alkali metal carbonate, alkali metal bicarbonate, alkali metal sequicarbonate, alkali metal borate, alkali metal silicate, and mixtures thereof. Alkali metal hydroxides are typically used where the detersive system requires strong cleaning action and highest pH. Silicates ($M_2O:SiO_2$ compounds having a ratio from about 2:1 to 1:3.6 wherein M is an alkali metal ion) are typically a reaction product between an alkali metal hydroxide and silica. Such silicates are primarily used as a source of alkalinity where moderate strength and pH are required. Carbonate and borate sources of alkalinity are typically used in compositions having an alkaline pH but do not require the strength of alkalinity of silicates or hydroxides.

Hardness Sequestering Agents

The detersive systems of the invention typically

contain a hardness sequestering agent to reduce the harmful effects of divalent and trivalent metal ions on the components of the detersive systems. The detersive systems of the invention can contain both organic and inorganic hardness sequestering agents. Such sequestering agents are typically in the form of polyanionic materials.

Inorganic hardness sequestering agents include alkali metal condensed phosphates in the form of pyrophosphate, tripolyphosphate, hexametaphosphate, etc. Organic hardness sequestering agents include polymeric and copolymeric compositions having pendent carboxylic acid functionality derived from carboxylic acid containing monomers such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid and mixtures thereof, etc.; alkali metal salts of organic substituted phosphonic acid and polyphosphonic acids, alkali metal salts of gluconic acid, alkali metal salts of ethylene diamine tetraacetic acid, alkali metal salts of nitrilotriacetic acid, and mixtures thereof.

Organic Materials

A variety of organic functional materials can be used in the detersive systems of the invention. Such functional materials include absorbents, adsorbents, antimicrobials, antioxidants, anti-soil agents, perfumes, dyes, binders, chelating agents, corrosion inhibitors, coupling agents, defoamers, dispersants, solubilizers, stabilizers, thickeners, and UV absorbers. Examples of such absorbents and adsorbents are microcrystalline cellulose, zinc ricinoleate, free-flowing malto dextrin, powdered acrylate copolymers, and others. Anti-soil or anti-soil redeposition agents that can be used include fatty acid amides, fluorocarbon surfactants, complex phosphate esters, styrene maleic anhydride copolymers, and cellulosic derivatives such as hydroxyethyl cellulose, hydroxypropyl cellulose, and others. Powder binders that can be used to aid in the formation of solid materials include microcrystalline cellulose, long chain lactate esters, long chain oleate esters, polyacrylamides, microcrystalline

waxes, polyvinyl alcohol resins, polyethylene, polyvinyl pyrrolidone, and others.

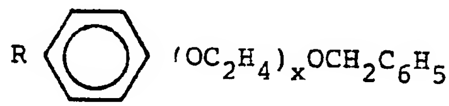
Defoamers that can be used in the detersive systems of the invention include high molecular weight C_{10-40} linear primary alcohols, polyalkylene glycols, well known silicone defoamers, certain acrylate copolymers, and others.

One important class of functional organic materials in the manufacture of detersive systems of the invention comprises organic surfactants. A wide variety of surfactants can be used in the detersive systems of the invention including anionic surfactants, zwitterionic surfactants (containing both anionic and cationic groups), cationic surfactants and nonionic surfactants. Anionic surfactants include alkyl carboxylate (sodium and potassium soaps), alkyl sulfate, alkyl ether sulfate, alkyl benzene sulfonate, alkyl sulfonate, sulfonated fatty acid ester, sulfosuccinate surfactant.

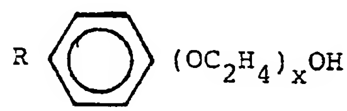
Nonionic surfactants typically in the form of compositions having polyalkylene oxide polymers as a portion of the surfactant molecule can be useful in the detersive systems of the invention.

Nonionic surfactants which are advantageously employed in the composition of this invention include, but are not limited to, the following polyoxyalkylene nonionic detergents: C_8-C_{22} normal fatty alcohol-ethylene oxide or propylene oxide condensates, i.e., condensation products of one mole of a fatty alcohol containing 8 to 22 carbon atoms with from 2 to 20 moles of ethylene oxide or propylene oxide; polyoxypropylene-polyoxyethylene condensates having the formula $HO(C_2H_4O)_x(C_3H_6O)_y$-H wherein $(C_2H_4O)_x$ equals at least 15% and $(C_3H_6O)_y$ equals 20-90% of the total weight of the compound; alkyl polyoxypropylenepolyoxyethylene condensates having the formula $RO-(C_3H_6O)_x(C_2H_4O)_yH$ where R is a C_1-C_{15} alkyl group and x and y each represent an integer of from 2 to 98; polyoxyalkylene glycols as described in U.S. Pat. No. 3,048,548; butylene oxide capped alcohol ethoxylates having the formula $R(OC_2H_4)_y(OC_4H_9)_xOH$

where R is a C_8-C_{18} alkyl group and y is from about 3.5 to 10 and x is an integer from about 0.5 to 1.5; benzyl ethers of polyoxyethylene condensates of alkyl phenols having the formula



where R is a C_6-C_{20} alkyl group and x is an integer of from 5 to 40; and alkyl phenoxy polyoxyethylene ethanols having the formula



where R is a C_8-C_{20} alkyl group and x is an integer of from 3 to 20.

Non-Surfactant Polyoxyalkylene Groups

Nonsurfactant polyalkylene oxide polymers are used in the manufacture of the detersive systems of the invention as a binder or as a casting agent in which the materials of the invention are blended with the casting agent at elevated temperatures and the cooling of the blended material solidifies the casting agent resulting in a stable cast solid. Such polyalkylene oxide polymers comprise homopolymers of ethylene oxide (EO), homopolymers of propylene oxide (PO), heteric EO/PO copolymers or block EO/PO copolymers, for example, those of molecular weight from 1,000 to 10,000, especially about 6,000 to 8,000. These materials are not to be considered as surfactant materials in the context of the present invention.

Additional Ingredients

The detersive systems of the invention can contain anti-foaming agents, typically in an amount of from about 0.001% to about 2%, preferably 0.05 to 1%. Such foam

suppressing or foam regulating agents include silicone compounds, phosphate esters, microcrystalline slack waxes, etc. In somewhat greater detail, preferred suds suppressing agents are silicone materials which are siloxanes having the formula

$$-[\underset{\textstyle R'}{\overset{\textstyle R}{\mathrm{Si}}}-O-]_x$$

wherein X is from about 20 to about 2,000 and R and R' are each independently selected from the group consisting of C_{1-20} alkyl or alkyl substituted aryl groups. Preferred groups include methyl, ethyl, propyl, butyl, and phenyl. Polydimethyl siloxanes having a molecular weight in the range of 200 to 200,000 and higher are useful suds controlling agents. Other suds suppressing agents include alkyl phosphate esters such as monostearyl phosphate and microcrystalline waxes having a melting point from about 65° C. to about 100° C. and having a molecular weight from 400 to about 1,000.

The detersive systems of the invention can contain neutral organic and inorganic fillers such as sodium sulfate and sodium chloride. Organic fillers that can be used in the invention include starch, sugars, alkylene glycols having from 1 to 10 carbon atoms, etc. Additionally the compositions can contain proteolytic and amylolytic enzymes, tarnish inhibitors such as benzotriazol, antibacterial agents, anti-soil redeposition agents, soil suspending agents, dyes, perfumes, and silicate, glass and aluminum tarnish suppressing agents.

Method of Casting the Detersive Systems

The components of the detersive systems are typically cast in a disposable container which also acts as a mold. The detersive system can be dispensed from the container or can be removed from the container prior to insertion in the

dispenser. Alternatively the detersive system components can be cast in a reusable mold wherein the cast material is removed from the mold and placed into a separate disposable container for shipment and use.

The detersive system can be cast in virtually any order of addition of materials to a mixing unit. Once uniform the material for casting is then placed in an appropriate mold.

A preferred mode of casting the material is to place the low molecular weight and water soluble materials into a mixing chamber in conjunction with any water used in the manufacture of the materials. Next the higher molecular weight or insoluble materials are slowly added to the contents of the mixing unit until a uniform suspension is obtained. Lastly the active halogen source can be added to the mixture. The mixture is carefully agitated at a slow rate such that the integrity of the encapsulate is not compromised.

Encapsulate

The encapsulated sources of halogen of this invention comprise a core of an active halogen compound and at least one coating layer. Preferably the encapsulated sources of halogen have a core and two or more coating layers. If one layer is used it preferably comprises an inorganic coating of a composition compatible with the halogen source, however certain coatings of a synthetic detergent can be used. If two layers are used the first layer comprises a typically inert or inorganic coating agent and the second layer comprises an organic layer or a synthetic detergent layer.

Halogen Source

The halogen releasing substances suitable as a core material include halogen components capable of liberating active halogen species such as a free elemental halogen or -OX- wherein X is Cl or Br, under conditions normally used in detergent-bleaching cleaning processes. Preferably the halogen releasing compound releases chlorine or bromine

species. The most preferred halogen releasing compound releases chlorine. Chlorine releasing compounds include potassium dichloroisocyanurate, sodium dichloroiso-cyanurate, chlorinated trisodium phosphate, calcium hypo-chlorite, lithium hypochlorite, monochloroamine, dichloro-amine, pentaisocyanurate, 1,3-dichloro-5,5-dimethyl hydantoin, paratoluene sulfondichloro-amide, trichloromelamine, N-chloromelamine, N-chlorosuccinimide, N,N'-dichloroazodi-carbonamide, N-chloro-acetyl-urea, N,N-dichlorobiuret, chlorinated dicyandiamide, trichlorocyanuric acid, and dichloroglycoluril.

Sodium dichloroisocyanurate, potassium dichloroiso-cyanurate and the dihydrates thereof are the most preferred oxidizing chlorine source suitable as a core substance. These materials are commercially available and may be obtained from sources such as Monsanto or Olin Corp.

Coating Materials

The coating on the active halogen source can be a single or multiple layer coating. Single layer coatings can comprise virtually any inert organic or inorganic coating material stable with a halogen source that is solid at room temperature. In the instance that a multiple layer coating is used, often the first layer is an inorganic layer where the second layer comprises an organic layer that can be drawn from a variety of sources.

Nearly any substance may be employed as the first coating so long as it is substantially halogen inert and is a solid at normal storage temperatures typically between 30° and 100° F. (-1° to 38° C.). The coating material is preferably inert with respect to the core material. If the inner coating material is potentially reactive with the core material, the core material may be initially coated with an inert material to prevent or retard any reaction between the core and this first coat, the initial coat acting as a chemical barrier between the core and the first and other layers. Useful inorganics in the coating material include alkalies such as sodium carbonate, sodium

bicarbonate, sodium sequicarbonate, sodium borate, potassium bicarbonate, potassium sequicarbonate, potassium borate, phosphates such as diammonium phosphates, monocalcium phosphate, tricalcium phosphate, calcium pyrophosphate, iron pyrophosphate, magnesium phosphate, monopotassium orthophosphate, potassium pyrophosphate, disodium orthophosphate, trisodium orthophosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium phosphate glass; neutral salts such as zeolites, sodium sulfate, sodium chloride, and talc; silicates and silicate hydrates such as sodium metasilicate, sodium sequisilicate, dry sodium/potassium silicate water glasses, sodium orthosilicate and mixtures thereof.

A useful initial inorganic coating compound for a halogen bleach core material to be used in a detergent composition would be an admixture of sodium sulfate and sodium tripolyphosphate. Sodium sulfate and sodium tripolyphosphate are relatively inert with respect to halogen bleaches and are components commonly blended into detergent compositions.

Outer Coating Materials

Nearly any substance may be employed as the outer coating material so long as it is solid at normal storage temperatures (typically between 30° and 100° F.). A nonexhaustive list of compounds which may be used as the second coat includes alkalies such as sodium carbonate, sodium bicarbonate, sodium sequicarbonate, sodium borate, potassium bicarbonate, potassium sequicarbonate, potassium borate, sodium sulfate hydrate, phosphates such as diammonium phosphates, monocalcium phosphate, tricalcium phosphate, calcium pyrophosphate, iron pyrophosphate, magnesium phosphate, monopotassium orthophosphate, potassium pyrophosphate, disodium orthophosphate, trisodium orthophosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium phosphate glass; neutral salts such as zeolites, sodium sulfate, sodium chloride, and talc; silicates and silicate hydrates such as sodium

metasilicate, sodium sequisilicate, dry sodium/potassium silicate water glasses, sodium orthosilicate; organic sequestering agents such as copolymers of vinylacetate and maleic anhydride, copolymers of acrylic acid and maleic anhydride, copolymers of maleic anhydride and itaconic acid, polyacrylic acid; and N-alkyl sulfonate, such as octyl sulfonate, sodium carboxymethyl celluloses, hydropropyl cellulose, hydroxyethyl ether of cellulose, hydroxypropylmethyl cellulose; C_{12} to C_{20} fatty acids such as stearic acid, palmitic acid, and n-alkanoic acids; paraffin waxes; microcrystalline waxes; C_{12} and greater primary and secondary solid alcohols; Pluronic surfactants with molecular weight between about 8,000 to about 16,500; primary and secondary alkyl sulfates; and alkali metal sulfonates and mixtures thereof. The preferred encapsulate uses an outer coating that is insoluble in the liquid composition prior to casting. After the detersive system is cast, the preferred encapsulates are water soluble to permit release of the halogen into the cleaning medium.

The synthetic detergent compound used in the coating must remain sufficiently solid at temperatures likely to be encountered during storage of the product, for example, temperatures of about 15 to 50° C., and also remain stable at temperatures likely to be encountered during processing of the product into end use mixtures, for example, temperatures of about 15 to 95° C.

Synthetic detergents that can be used include anionic, cationic, nonionic and amphoteric detergent compositions. Examples of anionic detergents useful in the detergent-bleach compositions of the invention are the higher alkyl mononuclear aromatic alkali-metal sulfates and sulfonates, and linear alkyl sulfates and sulfonates such as alkylbenzene sulfonates having about 9 to about 13 carbon atoms in the alkyl group wherein the alkyl group is derived from polypropylene as described by Lewis in U.S. Pat. No. 2,477,382, or wherein the alkyl group is a hexene dimer or trimer as in McEwan, U.S. Pat. No. 3,370,100, or wherein

the alkyl group is derived from alpha-olefins, as in Swenson, U.S. Pat. No. 3,214,462. Also there may be employed primary and secondary alkyl sulfates.

The soaps are included within the definition of anionic detergents as used herein. Examples of operable soaps soluble with the present invention are the sodium and potassium salts of acyclic monocarboxylic acids having chain lengths of about 8 to about 22 carbon atoms.

A particularly suitable synthetic detergent for use as a coating in the present invention is preoxidized sodium octyl sulfonate. The sodium octyl sulfonate may contain 1,2 alkane bisulfonate as a by-product of manufacture which does not affect the performance of sodium octyl sulfonate as a coating in the invention.

The organic compound coating is applied as a solution in a suitable solvent, water being preferred because of its compatibility with chlorine releasing agents, non-flammability, and non-toxicity.

The compositions of the present invention may be formulated with a detergent builder as a detergency aid, for example, those mentioned hereinafter, to provide a commercially valuable detergent-bleach composition.

Inorganic fillers suitable for coating agents include alkalies such as sodium bicarbonate, sodium sequicarbonate, sodium borate, potassium bicarbonate, potassium sequicarbonate, potassium borate; phosphates such as diammonium phosphate, monocalcium phosphate monohydrate, tricalcium phosphate, calcium pyrophosphate, iron pyrophosphate, magnesium phosphate, monopotassium orthophosphate, potassium pyrophosphate, disodium orthophosphate, dihydrate, trisodium orthophosphate, decahydrate, tetrasodium pyrophosphate, sodium tripolyphosphate, sodium phosphate glass; neutral soluble salts such as sodium sulfate and sodium chloride; silicates; organic sequestering agents; and anti-redeposition agents.

When carrying out the process of the instant invention, the protective encapsulate materials or coatings

of the invention are conveniently applied using fluidized bed encapsulating equipment. Such equipment comprises a coating chamber or cylindrical tower wherein the coating or encapsulation of the particles is accomplished. An unexpanded bed of the particles to be coated is introduced into the equipment. A nozzle constituting a spraying means is disposed within the equipment and adapted to be adjusted vertically so that the liquid coating material discharged in a downwardly diverging three-dimensional spray pattern would just cover the upper surface area of the bed.

The coating solution is contained in a vessel and is fed to the nozzle. Fluidizing gas (typically air) passes into the fluidized bed area. The fluidized gas is heated or cooled if required, in order to maintain the fluidizing gas within a desired temperature range.

A known weight of particles of a halogen source to be coated is placed in the equipment. Air is caused to flow into the fluidized bed thereby expanding the layer of particles, and maintaining the particles in continuous motion within the volume defined by the expanded bed, thus forming a fluidized bed. A solution of a coating substance is sprayed through the nozzle on the fluidized bed of particles until all particles in the bed are completely coated. Particles coated by the above-described procedure are completely encapsulated with a continuous coating, and are free-flowing a .d non-agglomerated.

It is important that each particle be fully covered to prevent the oxidizing halogen source from reacting in the detersive system environment.

When it is desired to apply an initial coating of a coating agent and a subsequent coating of a synthetic detergent, the double coating may be conducted in a single fluidized bed either by applying the first coat, emptying the solution tank, filling the solution tank with the second coating solution and then applying the second coat; or with a dual coating solution inlet to the nozzle, the fluidized particles in the bed first being coated with the

coating agent contained in a solution tank, this first coating being allowed to dry and then a second coating of the synthetic detergent contained in a second solution tank being applied, both coatings being conducted in accordance with the previous discussion on the operation of the fluidized bed.

A third method of applying a double coating in a fluidized bed is to coat the core particles with the coating agent in a first fluidized bed apparatus. The coated material is then allowed to dry and placed in a second fluidized bed apparatus, wherein the encapsulated product produced in the first fluidized bed is coated with a second coating solution of a synthetic detergent. The fluidized bed operation is conducted in accordance with the prior discussion of the operation of the fluidized bed.

Before removal of the encapsulated oxidizing chlorine source from the fluidized bed the temperature in the bed can be increased so as to drive off any solvent remaining in the encapsulate. However, the temperature must remain below the melting temperature of the encapsulant and below the degradation temperature of the encapsulated core and coatings.

The encapsulated halogen bleach sources of the present invention comprise about 20 to 90 wt-% halogen bleach source core and about 10 to 80 wt-% coating when a single coating is utilized, and about 20 to 90 wt-% halogen bleach source core, about 0.5 to 50 wt-% inorganic coating agent first coat, and about 5 to 70 wt-% synthetic coating when a double coating is utilized.

More particularly, the single coated halogen bleach source comprises about 30 to 80 wt-% halogen bleach source core and about 20 to 70 wt-% synthetic coating and most particularly about 40 to 55 wt-% halogen bleach source core and 45 to 60 wt-% synthetic coating.

A more preferred embodiment of the double coated halogen bleach source comprises about 30 to 80 wt-% halogen bleach source core, about 5 to 50 wt-% inorganic coating

agent first coating, and about 5 to 50 wt-% synthetic coating. In a most preferred embodiment, the encapsulate comprises about 30 to 60 wt-% chlorine bleach source core, about 15 to 45 wt-% inorganic coating agent first coating, and about 10 to 35 wt-% detergent second coating.

Dispensing

The cast solid detersive systems of the invention can be dispensed from a manual or automatic dispenser in which a stream of water is contacted with a surface of the cast material providing a concentrate that is directed to a use location.

The cast material can be contained in a disposable container and inserted into the dispenser in that form. Alternatively the cast material can be manually removed from a disposable container directly into a dispenser wherein the stream of water is contacted with at least one surface of the material. Typical dispensers are mechanical apparatus containing a nozzle for directing a stream of water onto the solid cast material. The dispenser typically comprises a housing containing the internal working parts. The housing typically includes a storage portion wherein the mass of the solid block detersive system can be supported. The dispenser contains typically a support means upon which the cast material is placed. The support is typically horizontally mounted within the dispenser and maintains the block material in position adjacent to the spray. The preferred support comprises a screen mounted to the inner walls of the housing at a position fixed above the spray such that the spray contacts the majority of the solid cast detersive system. The spray-forming nozzle is connected to a pressurized source of water by means of a supply line. The spray is controlled by a device that can demand the addition of the concentrate made by spraying water on the cast material. Upon the receipt of demand, water flow is directed through the supply line and nozzle onto substantially the entire lower surface of the cast material at pressures typically

greater than 10 psi. Heated water can be used depending on the formulation. The use of heated water, all else being equal, increases the rate of dispensing. The detersive system passes in solution form through the support screen and is directed by underlying collector portion of the housing to an outlet port and through a conduit to a utilization point. The utilization point can be a warewashing machine, a station for charging containers such as buckets or other apparatus with a concentrate for dissolution with additional quantities of water, or other use positions.

Alternatively the dispensing apparatus can be manually operated such that a measured amount of concentrate can be produced by manually triggering the spray onto the cast material.

We have found that the stability of the chlorine source in the presence of the organic compositions relates to the quantity of free water in the cast material. We have found that the detersive systems during manufacture require some water for processing. Preferably all water present in the detersive system after casting is in the form of bound water or water of hydration or complexed water which is sequestered and removed from reactivity with the components. Free water is water available for reaction with the encapsulated chlorine material and can provide a medium of reaction between released chlorine and any organics present in the cast material. We have found that maintaining the concentration of free water below about 10 wt-% can aid in preserving the availability of chlorine in the cast material over a substantial period of time, preferably maintaining the concentration of free water at less than 5 wt-% or most preferably less than 2 wt-% can be very effective in maintaining the stability of the material.

Example I

Chlorinated General Purpose Cleaner

Into a stainless steel jacketed tank equipped with a

variable speed turbine agitator was charged 10 parts of soft water which was heated to 170° F. Into the mixed water was added 20 parts of a polyethylene glycol (CARBOWAX 8000, Union Carbide) at a sufficient rate to dissolve the CARBOWAX in the water. Agitation was ended and into the tank was placed 22 parts of a linear alkyl benzene sulfonate, 4 parts of a polyacrylic acid polymer (GOODRITE K-7058D, B. F. Goodrich), 14.5 parts of a powdered sodium tripolyphosphate, and 1 part of a granular sodium tripolyphosphate, 14 parts of anhydrous sodium metasilicate and 6 parts of sodium bicarbonate. The product was cooled to a temperature below 145° F. Next, 8.5 parts of an encapsulated sodium isocyanurate (of Example II) is added to the tank and the contents of the tank are carefully agitated at a temperature below 145° F. in a manner such that the encapsulate is evenly distributed throughout the product. The material is drawn from the tank and 2 lbs. of the warm liquid material is placed in polyethylene containers. The containers and their contents are cooled in an air chiller for 12-15 minutes at a temperature less than 10° F. and are solidified.

Example II

The encapsulated sodium dichloroisocyanurate used in Example I was prepared as follows. Into a cylindrical fluidized bed encapsulating machine was placed 61.25 parts of sodium dichloroisocyanurate. The particles were fluidized and suspended in air by an upwardly moving stream of air at a temperature of about 90° C. Onto the heated suspended particulate was sprayed a solution comprising in 68.97 parts of soft deionized water, 16.5 parts of sodium sulfate and 5.5 parts of sodium tripolyphosphate. The addition of this solution creates a first inorganic layer of mixed sodium sulfate and sodium tripolyphosphate. After the complete addition of the inorganic layer, a solution comprising 49.62 parts of a sodium linear alkyl sulfonate in 49.62 parts of soft water is then sprayed on the fluidized particle. This second step created an organic

encapsulate layer on the exterior of the particle. Substantially all free water (about 151.5 parts were removed) was removed during encapsulation.

Example III

A chlorinated solid laundry detergent was made according to the following procedure. Into a stainless steel mixing tank equipped with heating and cooling and a variable speed turbine agitator was placed 20 parts of a nonylphenol ethoxylate having an average of 9.5 moles of ethylene oxide, and 0.6 part of hexylene glycol. The mixer is begun and into the tank is charged 11.35 parts of a polyethylene glycol (CARBOWAX 8000, Union Carbide) at a rate such that the polyethylene glycol melts and dissolves in the liquid phase. In a separate container 2.3 parts of soft water, 0.1 part of a fluorescent brightener and 0.004 part of a blue dye were mixed and then charged to the tank. The temperature of the charged materials was permitted to fall below 150° F. In a separate dry blender 0.5 part of carboxymethyl cellulose, 27.246 parts of sodium tripolyphosphate powder and 9.4 parts of anhydrous sodium metasilicate were dry blended. The dry blend was slowly added to the liquid phase in the mixing tank. After uniformity was reached, 0.25 part of a fragrance was added. The mixture was cooled and to the carefully agitated mixture was added 19 parts of a chlorinated isocyanurate manufactured in Example IV with 5 parts of sodium carbonate. The agitation was controlled such that the encapsulate was just distributed throughout the product and terminated. The material was packaged in 4 lb. aliquots in polyethylene tubs and cooled until solid.

Example IV

Using the procedure of Example II the following encapsulate was prepared.

Ingredient	Parts by Weight
Core:	
Sodium dichloroisocyanurate	63.2
Coating 1:	
Sodium sulfate	25.8
Sodium tripolyphosphate	8.6
Soft water	103.0
Coating 2:	
Hydroxypropyl cellulose	4.9
Soft water	98.4
Water removed during encapsulation	203.9

Example V

Using the procedure of Example II an encapsulated chlorine source was prepared using the following ingredients.

Ingredient	Parts by Weight
Core:	
Sodium dichloroisocyanurate	80.65
Coating 1:	
Sodium sulfate	14.73
Sodium tripolyphosphate	4.33
Soft water	58.68
Coating 2:	
Carboxymethyl cellulose	5.00
Soft water	88.80
Water removed during encapsulation	351.27

Example VI

Using the procedure of Example II an encapsulated chlorine source was prepared using the following ingredients.

Ingredient	Parts by Weight
Core:	
Sodium dichloroisocyanurate	63.2
Sodium sulfate	25.8
Coating 1:	
Sodium tripolyphosphate	8.6
Soft water	103.0
Coating 2:	
Hydroxyethyl cellulose	4.9
Soft water	98.3
Water removed during encapsulation	203.9

Example VII

An encapsulated chlorine source was prepared using the procedure of Example II using the following ingredients.

Ingredient	Parts by Weight
Core:	
Sodium dichloroisocyanurate	63.2
Coating 1:	
Sodium sulfate	25.8
Sodium tripolyphosphate	8.6
Soft water	103.0
Coating 2:	
Methyl cellulose	4.92
Soft water	245.92
Water removed during encapsulation	351.46

Example VIII

A solid chlorinated fabric softening laundry detergent was prepared following the procedure of Example III using the following ingredients.

Ingredient	Parts by Weight
Nonylphenol ethoxylate with 9.5 moles ethylene oxide	26.39
Hexylene glycol	1.17
Polyethylene glycol	14.66
Soft water	2.25
Dye	0.08
Sodium tripolyphosphate	26.39
Sodium metasilicate	3.81
Quaternary ammonium fabric softener	2.25
Encapsulate of Example VI	23.00

Example IX

Example VI was repeated with the encapsulate of Example II.

Example X

Example VIII was repeated with the encapsulate of Example V.

Example XI

Example VIII was repeated with the encapsulate of Example VII.

Table 1

Active Chlorine Stability

Percent Active Chlorine Retained After Storage at 100° for Two Weeks

Preparation	Percent Retained
Example VIII	67.2
Example IX	57.5
Example X	62.8
Example XI	85.2

Example XII

Chlorinated General Purpose Cleaner

Into a stainless steel mix tank equipped with heating and cooling equipment and a variable speed turbine type

agitator was added 10 parts of water and 22 parts of polyethylene glycol (CARBOWAX 8000). The glycol was added at a rate such that it was melted and fully mixed upon addition. Into the heated solution was added 20 parts of a linear alkyl sulfonate, 4 parts of a polyacrylate polymer, 15.5 parts of sodium tripolyphosphate, 14.0 parts of sodium metasilicate, and 6 parts of sodium bicarbonate. The contents of the mixer were agitated until uniform and into the mixer was added 8.5 parts of the encapsulate of Example II. The contents of the mixer were carefully agitated until just uniform. The material manufactured above had a chlorine stability of 106.06% chlorine retained at 100° F. for two weeks of storage.

Table 2

Dispensing Characteristics of Product of Example XII

Temperature	Grams Dispensed (Average of 5 Tests) At 30 psi	At 50 psi
120°	34.338	53.735
130°	38.72	59.2
140°	50.68	66.184
150°	55.44	81.7

The data in Table 2 shows that the product of Example XII is easily dispensed using warm water at commonly available temperatures at commonly available pressures at most end use sites. The product can easily be dispensed for any typical end use by controlling either pressure, temperature or dispensing time.

The product was dispensed by placing the material in a dispenser using a 30-second cycle at either 30 or 50 psi and at temperatures ranging from 120-150° F.

A useful dispenser is shown in FIGURE 1. Referring to Fig. 1, there is generally disclosed a dispenser having a container or housing 20. The housing has a generally cylindrical upper storage portion 21 having a cylindrical

inner wall 22. The wall 22 defines an internal cavity 23. The upper terminous of the storage portion 21 defines an access port 24 into cavity 23 of storage portion 21.

Inner wall 22 of housing 20 converges in the downward direction, defining a lower funnel-shaped collector portion 25 of housing 20. Inner wall 22 of housing 20 is configured to form an annular flange at 26 circumferentially extending around inner wall 22 of housing 20 at the juncture of upper storage portion 21 and lower collector portion 25. The lower terminous of collector portion 25 defines an outlet port 27 from internal cavity 23 for passage therethrough of solution collected by collector portion 25. Outlet port 27 has a hose clamp extension 28 having a plurality of annular ribs configured for engaging the inner walls of a connecting hose or conduit 29.

The outlet port 27 may be directly connected with the wash chemical solution utilization point by conduit 29 and feed thereto by gravity as it is created or feed thereto by a wash chemical solution pump 30 placed in conduit 29.

Housing 20 may be constructed of any suitable material which is capable of withstanding exposure to cleaning solutions, and is preferably configured of stainless steel or molded plastic material. The housing 20 can be constructed of a transparent or translucent material to allow the operator to see at a glance the amount of wash chemical in storage portion 21 and if dispenser 20 needs to be refilled. If housing 20 is not made of a transparent or translucent material, preferably a portion of storage portion 21 is made transparent or translucent to aid in determining when dispenser 20 should be refilled. A pair of mounting plates 32 are connected to and extend rearwardly from the outer surface of housing 20 for securely mounting housing 20 to a vertical side wall.

A door 34 is sized to extend entirely across and to sealingly close access port 24. Door 34 is pivotally mounted at 35 for pivotal motion between a closed and

opened position. The lower collector portion 25 of housing 20 has an outwardly projecting coupling portion 36 extending from collector portion 25 adjacent outlet port 27 of collector portion 25. A tube fitting insert 37 is secured within coupling projection 36 and projects through inner wall 22 of collector portion 25 of housing 20. A spray-forming nozzle 38 is threaded into the end of tube insert 37 and is axially aligned within inner cavity 23 of housing 20 in a direction so as to direct an upwardly projected spray pattern therefrom. Tube fitting insert 37 is provided with an O-ring seal 39.

A horizontal support screen 40 is mounted in resting engagement upon annular flanged portion 26 of housing 20. Support screen 40 nas about 1 inch square openings in order to support a solid block of detersive system 80 without significantly interfering with the impingement of water sprayed from nozzle 38 onto the lower surface of water sprayed from nozzle 38 onto the lower surface 81 of the detersive system 80 (i.e., the surface in contact with support screen 40).

A 1/4 to 1/20 inch (0.63 to 0.13 cm) lower screen 41 is placed in collector portion 25 of housing 20 between spray nozzle 38 and outlet port 27 to catch any undissolved chunks of wash chemical 80 small enough to pass through support screen 40. This prevents small chunks of chemical 80 collecti g in outlet port 27 or conduit 29 and blocking the flow of concentrated wash chemical solution out of dispenser 20.

A water supply inlet pipe 42 is connected to tube insert 37 and is in communication therewith for providing a source of water flow to spray-forming nozzle 38. Water supply line 42 passes through one of the mounting plate members 32 and receives structural support therefrom. A siphon breaker 43 interrupts water supply, line 42. A safety switch 50 is mounted to door 34 for movement therewith and senses the operative position of door 34 relative to access port 24 of housing 20. In the preferred

embodiment, safety switch 50 comprises a mercury actuated switch.

FIGURES 2 and 3 represent an embodiment of the product format for the cast detersive systems of the invention. The solid cast detersive system of the invention is packaged in a closable container 200 which comprises a lid 210 and a lower container section 211. The lid 210 can be made of a variety of materials including paper, film, foil, etc. The lower container can also be made of a variety of materials, however thermoplastic deformable material is preferred. The lid 210 is adhered to the container 211 through a releasable layer 212 disposed between the lid and the container.

FIGURE 3 shows a side view of the cast detersive system within its container. In use lid 210 is peeled from the top of the lower portion revealing the upper surface of the cast material 80. The container as a whole without the lid can be inserted into the dispenser. Alternatively the container body 211 if made of a deformable material can be flexed for the purpose of removing the cast material 80 in a solid block which can then directly be inserted into the dispenser for contact with a water stream.

While the foregoing discussion, Examples and data provide a basis to understand the invention, many embodiments of the invention can be made without departing from the spirit and scope of the invention. Thus the invention resides in the claims hereinafter appended.

WHAT IS CLAIMED IS:

1. A solid cast, active halogen-containing, storage-stable, detersive system comprising:

(a) an effective detersive amount of a source of alkalinity;

(b) an effective amount of a hardness sequestering agent;

(c) about 5 to 60 wt-% of an encapsulated source of active halogen; and

(d) about 5 to 50 wt-% of a polyalkylene oxide polymer;

wherein, in the cast composition, the halogen available from the source of active halogen is storage stable in the presence of the polyalkylene oxide polymeric composition.

2. The detersive system of claim 1 wherein the halogen is chlorine.

3. The detersive system of claim 2 wherein there is 15 to 30 wt-% of the encapsulated source of active chlorine.

4. The detersive system of claim 2 wherein there is 15 to 50 wt-% of the encapsulated source of active chlorine.

5. The detersive system of claim 2 wherein there is 20 to 35 wt-% of the source of encapsulated active chlorine.

6. The detersive system of claim 2 wherein the encapsulate comprises 1 to 80 wt-% of a source of active chlorine and 99 to 20 wt-% of an encapsulating layer.

7. The detersive system of claim 6 wherein the encapsulating layer comprises a synthetic anionic surfactant.

8. The detersive system of claim 6 wherein the encapsulating layer comprises 10 to 90 wt-% of a first inorganic layer and 90 to 10 wt-% of a second organic layer.

9. The detersive system of claim 8 wherein the organic encapsulating layer comprises a cellulosic layer, a

synthetic anionic surfactant or mixtures thereof.

10. The detersive system of claim 9 wherein the cellulosic layer comprises methyl cellulose, a hydroxyalkyl cellulose, or mixtures thereof.

11. The detersive system of claim 2 wherein the source of active chlorine is selected from the group consisting of trichloroisocyanuric acid, potassium dichloroisocyanurate, sodium dichloroisocyanurate, sodium dichloroisocyanurate dihydrate, and mixtures thereof.

12. The detersive system of claim 1 wherein the polyalkylene oxide polymeric composition comprises a polyethylene oxide polymer, a polypropylene oxide polymer, or an ethylene oxide/propylene oxide block copolymer.

13. The detersive system of claim 12 wherein the alkylene oxide polymer comprises a nonionic surfactant.

14. The detersive system of claim 13 wherein the nonionic surfactant comprises a block copolymer containing at least one ethylene oxide block and at least one propylene oxide block.

15. The detersive system of claim 14 wherein the nonionic surfactant comprises an alkyl phenol alkoxylate wherein the alkyl group is a C_{1-12} alkyl and the alkoxylate comprises 2 to 24 moles of ethylene oxide.

16. The detersive system of claim 1 wherein the hardness sequestering agent comprises an organic hardness sequestering agent or an inorganic hardness sequestering agent.

17. The detersive system of claim 16 wherein the organic hardness sequestering agent comprises a polyacrylic acid, an organic phosphonate, or mixtures thereof.

18. The detersive system of claim 16 wherein the inorganic hardness sequestering agent comprises a condensed phosphate hardness sequestering agent.

19. The detersive system of claim 18 wherein the condensed phosphate comprises an alkali metal tripolyphosphate sequestering agent.

20. The detersive system of claim 1 wherein the

source of alkalinity comprises an alkali metal hydroxide or an alkali metal silicate having an $M_2O:SiO_2$ ratio of about 2:1 to 1:3.6 wherein M is an alkali metal.

21. The detersive system of claim 1 wherein the source of alkalinity comprises an alkali metal carbonate, an alkali metal bicarbonate, an alkali metal borate and mixtures thereof.

22. The detersive system of claim 1 which additionally comprises an anionic surfactant.

23. The detersive system of claim 22 wherein the anionic surfactant comprises an alkyl sulfonate, an alkyl sulfate, an alkyl benzene sulfonate, an alkyl benzene sulfate, or mixtures thereof.

24. A solid, cast, stable, chlorine-cont:ining laundry detergent comprising:

(a) about 0.1 to 50 wt-% of a soil-removing nonionic surfactant;

(b) about 0.1 to 95 wt-% of a source of alkalinity;

(c) an effective amount of a hardness sequestering agent;

(d) about 5 to 60 wt-% of an encapsulated chlorinated isocyanurate compound; and

(e) about 5 to 50 wt-% of a polyalkylene glycol casting agent;

wherein, in the cast laundry detergent composition, the available chlorine is storage stable in the presence of the nonionic surfactant and the polyalkylene glycol casting agent.

25. The detergent of claim 24 wherein there is 15 to 30 wt-% of the encapsulated source of active chlorine.

26. The detergent of claim 24 wherein there is 20 to 25 wt-% of the source of encapsulated active chlorine.

27. The detergent of claim 24 wherein the encapsulate comprises 1 to 80 wt-% of a source of active chlorine and 99 to 20 wt-% of an encapsulating layer.

2:. The detergent of claim 27 wherein the

encapsulating layer comprises a synthetic anionic surfactant.

29. The detergent of claim 27 wherein the encapsulating layer comprises 10 to 90 wt-% of a first inorganic layer and 90 to 10 wt-% of a second layer comprising an organic encapsulating layer.

30. The detergent of claim 29 wherein the organic encapsulating layer comprises a cellulosic layer, a synthetic anionic surfactant or mixtures thereof.

31. The detergent of claim 30 wherein the cellulosic layer comprises methyl cellulose, a hydroxyalkyl cellulose, or mixtures thereof.

32. The laundry detergent of claim 24 wherein the detergent additionally comprises an effective amount of a soil anti-redeposition agent.

33. The detergent of claim 32 wherein the soil anti-redeposition agent comprises a carboxymethyl cellulose composition.

34. The detergent of claim 24 wherein the detergent additionally comprises a dye, a perfume, an anti-redeposition agent, a brightener or mixtures thereof.

35. The detergent of claim 24 wherein the chlorinated isocyanurate compound is selected from the group consisting of trichloroisocyanuric acid, potassium dichloroisocyanurate, sodium dichloro isocyanurate, sodium dichloro isocyanurate dihydrate, and mixtures thereof.

36. The detergent of claim 35 wherein the nonionic surfactant comprises a block copolymer containing at least one ethylene oxide block and at least one propylene oxide block.

37. The detergent of claim 36 wherein the nonionic surfactant comprises an alkyl phenol alkoxylate wherein the alkyl group is a C_{1-12} alkyl and the alkoxylate comprises 2 to 24 moles of ethylene oxide.

38. The detergent of claim 24 wherein the hardness sequestering agent comprises an organic hardness sequestering agent or an inorganic hardness sequestering

agent.

39. The detergent of claim 38 wherein the organic hardness sequestering agent comprises a polyacrylic acid, an organic phosphonate, or mixtures thereof.

40. The detergent of claim 38 wherein the inorganic hardness sequestering agent comprises a condensed phosphate hardness sequestering agent.

41. The detergent of claim 40 wherein the condensed phosphate comprises an alkali metal tripolyphosphate sequestering agent, an alkali metal carbonate, an alkyl metal bicarbonate, and mixtures thereof.

42. The detergent of claim 24 wherein the source of alkalinity comprises an alkali metal hydroxide or an alkali metal silicate having an $M_2O:SiO_2$ ratio of about 2:1 to 1:3.6 wherein M is an alkali metal.

43. The detergent of claim 24 which additionally comprises an anionic surfactant.

44. The detergent of claim 24 which additionally comprises a quaternary fabric softener.

FIG. 1

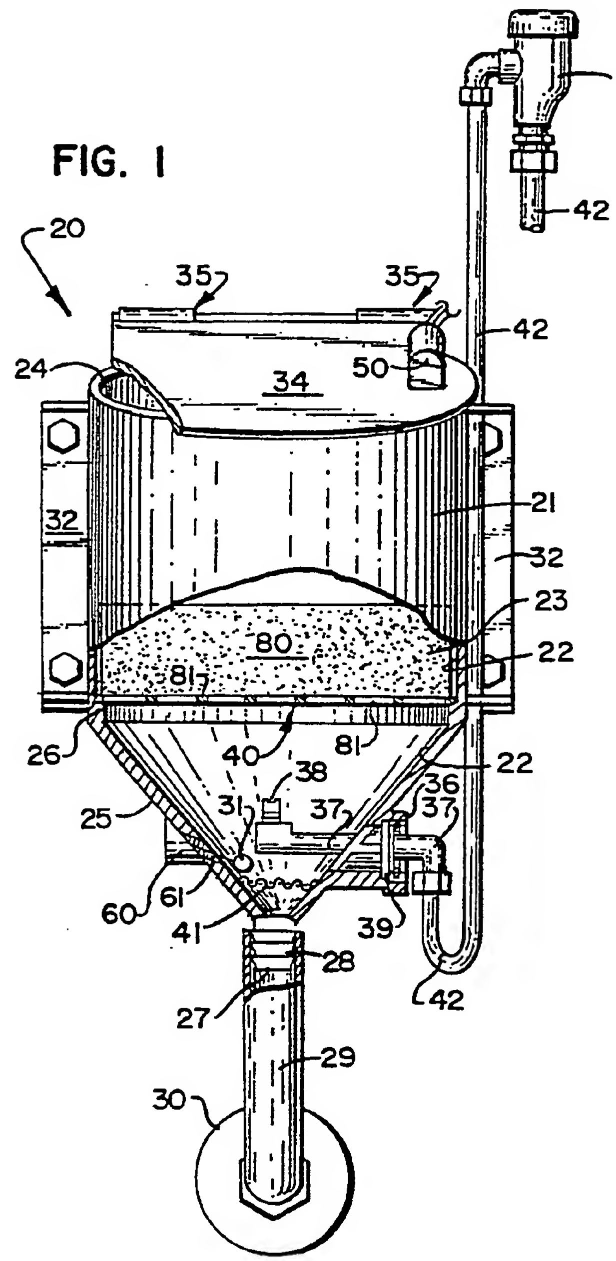

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FIG. 2

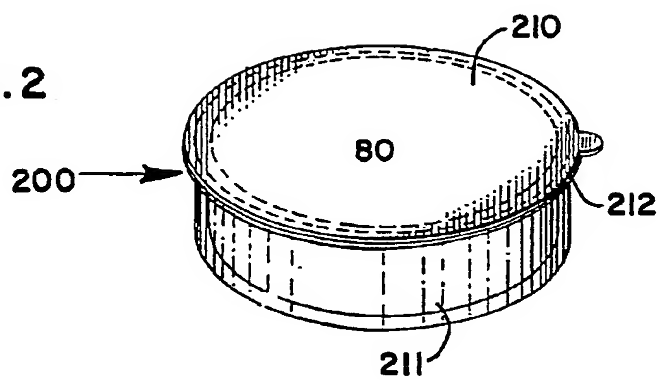
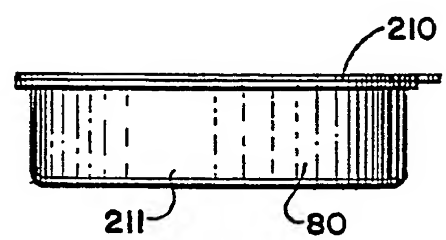


FIG.3



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/03313

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 11 D 3/395, C 11 D 17/00, C 11 D 3/37

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	C 11 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A, 0307587 (ECOLAB INC.) 22 March 1989 see page 6, lines 13-45; examples and claims --	1-43
A	EP, A, 0003769 (ECONOMICS LAB.) 5 September 1979 see claims --	1
A	EP, A, 0264043 (HENKEL) 20 April 1988 see claims --	1
A	US, A, 3637509 (W.R. BRENNAN) 25 January 1972 see claims --	1
A	US, A, 4136052 (L.R. MAZZOLA) 23 January 1979 see claims --	1
A	EP, A, 0298222 (ECOLAB INC.) 11 January 1989 ./.	1

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th October 1989	10 NOV. 1989
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	T.K. WILLIS

International Application No. PCT/US 89/03313

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	see claims --------	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 8903313 SA 30516

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/11/89 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A- 0003769	05-09-79	BE-A- 904138	15-05-86
		CA-A- 1125621	15-06-82
		JP-A- 54152007	29-11-79
		US-A- 4569781	11-02-86
		US-A- 4569780	11-02-86
		US-E- RE32763	11-10-88
		US-E- RE32818	03-01-89
EP-A- 0264043	20-04-88	DE-A- 3634812	14-04-88
US-A- 3637509	25-01-72	None	
US-A- 4136052	23-01-79	US-A- 4078099	07-03-78
		AU-B- 508961	17-04-80
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		JP-A- 1031899	02-02-89

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82